

members of the n-alkane family.⁶ The solubility of n-alkanes falls by a factor of around 3 for each additional CH₂ group; this fall is reflected in the rates shown in Fig 1. Plots of ΔG° and ΔH° as a function of the number (*n*) of carbons in the alkane chain are linear, confirming that a group contribution law applies, in that each additional CH₂ group adds a constant amount of energy to the process.

The rate of ripening is dependent on the solubility of the oil in the aqueous phase, and so micelles (through solubilisation) might be expected to increase the rate. The rate of ripening was measured as a function of SDS concentration (0–2%) at several sodium chloride concentrations (0–0.2 mol dm⁻³). The presence of sodium chloride reduced the interfacial tension in the emulsion, and, to remove this effect, rates were normalised to that at the CMC of the SDS/ pentanol mixture (0.18% in the absence of added electrolyte). This allowed the effects of micelles to be studied in isolation.

The presence of micelles has relatively little effect on the rate of ripening, with the rate typically increasing by a factor of around 2 at 2% SDS; the rate is still mainly governed by the alkane aqueous solubility. For the micelles to affect the rate significantly they must rapidly absorb the material dissolving from small droplets into the micellar core and transport them to large droplets for redeposition. The small dependence of rate on micellar concentration suggests that the oil is not rapidly taken up into the micelles – this may be due to electrostatic repulsion between the micelles and SDS molecules adsorbed on the droplets preventing close approach. Addition of sodium chloride initially increases the effect of the micelles through depression of the electrostatic repulsion between the droplets and the micelles. At higher concentrations this effect decreases as the increased solubilisation capacity of the micelles competes with the Ostwald ripening.

In summary – temperature-insensitive micro-emulsions may be prepared using ionic/ non-ionic surfactant mixtures. Simple modelling of the natural curvature leads to a predictive model for the optimum composition. Dilution of O/W microemulsions containing a single oil leads to droplet growth by Ostwald ripening. While the rate is sensitive to temperature, micellar or electrolyte concentration, the dominant factor is the aqueous solubility of the oil.

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Drift reduction and droplet-size in sprays containing adjuvant oil emulsions

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Abstract: The droplet-sizes and drift produced by sprays containing dilute oil-in-water emulsions of various vegetable and mineral oil adjuvants were measured in wind-tunnel experiments. When compared with water or a surfactant solution, both types of oil adjuvant reduced the proportion of small driftable droplets and, hence, reduced measured spray drift. Vegetable oils were more effective at drift reduction than the mineral oil. Spray drift tended to increase with increasing oil concentration and decreasing emulsifier content.

Keywords: adjuvant oils; oil-in-water emulsions; spray drift; droplet-size; spray quality

Emulsions of adjuvant oils are often added to pesticide formulations to enhance their biological activity, especially when the pesticides are used at reduced dose rates. However, their influence on the safety and efficiency of the spray application process is poorly understood. In addition, there are growing concerns about the biodegradability of mineral oil adjuvants and substitutes based on renewable and more environmentally acceptable vegetable oils are becoming of increasing importance.

In the present work, we have measured the drift potential of emulsion formulations of three oils supplied by Croda Chemicals Ltd, UK: alkali-refined rapeseed oil (ARRO), methylated rapeseed oil (MRO) and a mineral oil (MO). These were selected from a short list of seven oils (one mineral, three rapeseed and three linseed), based on their performance in biological efficacy experiments.¹ All oils were formulated as ECs containing 50 g litre⁻¹ of a 5 EO oleyl alcohol as emulsifier. Oil concentrations in the spray liquid were 2, 10 and 20 g litre⁻¹, and 0.2 g litre⁻¹ sodium fluorescein was added as a tracer for quantification of drift. Comparisons were made with water, the emulsifier alone and a 1 g litre⁻¹ aqueous solution of a 10 EO nonylphenol surfactant ('Agral', ex Zeneca, UK).

Airborne spray drift was measured 2 m down-wind of a single, stationary 11002 nozzle (Lurmark, UK) atomiser with an output of 0.64 litre min⁻¹ in a wind speed of 2.5 m s⁻¹. The nozzle was positioned so that its long axis was at 90° to the wind direction. Drift was collected according to an established protocol² on five

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Table 1. Effect of oil-based adjuvants on in-flight PDPA droplet spectra from a 11002 nozzle delivering 0.64 litre min^{-1a}

Spray liquid (g litre ⁻¹)	V(10) (μm)	VMD ^b (μm)	V(90) (μm)	NMD ^c (μm)	VMD/NMD ratio	Volume	Volume >250μm (%)	Velocity (ms ⁻¹)
Water	139 (2.71)	267 (2.46)	390 (2.47)	52 (1.99)	5.15 (0.18)	4.42 (0.21)	56.1 (1.03)	2.27 (0.01)
Agral (1)	128 (1.57)	247 (1.25)	364 (2.86)	49 (0.13)	5.04 (0.03)	5.75 (0.17)	48.5 (0.48)	2.33 (0.03)
Emulsifier (0.125)	173 (1.15)	293 (0.65)	421 (2.80)	121 (3.37)	2.43 (0.06)	1.64 (0.09)	66.3 (0.27)	2.85 (0.02)
Emulsifier (0.5)	174 (2.48)	289 (3.15)	406 (6.89)	118 (3.28)	2.45 (0.04)	1.67 (0.05)	65.1 (0.82)	2.88 (0.03)
Emulsifier (1)	176 (0.83)	290 (2.10)	395 (2.63)	113 (1.83)	2.56 (0.05)	1.62 (0.05)	66.0 (0.77)	2.84 (0.03)
MO (2.5)	165 (1.66)	282 (3.31)	413 (15.03)	88 (0.87)	3.19 (0.02)	2.32 (0.07)	62.3 (0.64)	2.49 (0.02)
MO (10)	167 (1.87)	315 (5.54)	503 (25.0)	74 (2.57)	4.28 (0.08)	2.27 (0.12)	65.1 (1.01)	2.46 (0.02)
MO (10)+Agral (1)	136 (1.10)	260 (5.23)	405 (13.20)	52 (1.19)	4.97 (0.03)	4.81 (0.21)	52.8 (1.46)	2.31 (0.03)
ARRO (2.5)	169 (4.78)	295 (4.31)	425 (2.72)	109 (2.66)	2.70 (0.03)	1.84 (0.16)	65.5 (1.14)	2.66 (0.04)
ARRO (10)	187 (5.50)	326 (4.66)	518 (26.67)	88 (4.55)	3.72 (0.24)	1.57 (0.10)	73.0 (1.30)	2.50 (0.05)
MRO (2.5)	187 (1.77)	305 (1.03)	450 (3.01)	117 (2.99)	2.60 (0.07)	1.34 (0.04)	71.0 (0.26)	2.75 (0.01)
MRO (10)	180 (2.24)	303 (3.23)	437 (8.80)	108 (5.81)	2.82 (0.14)	1.58 (0.15)	68.1 (0.88)	2.70 (0.03)
MRO (10)+Agral (1)	179 (4.29)	303 (7.28)	466 (22.77)	85 (3.52)	3.54 (0.18)	1.76 (0.13)	68.6 (2.28)	2.55 (0.10)

^a Mean of three replicates with standard errors in parentheses.

^b VMD=volume median diameter. Droplet diameter that divides the spray volume into two equal parts; 50% is in droplets larger than this diameter and 50% smaller.

^c NMD=number median diameter. Droplet diameter that divides the droplets into two equal parts; 50% are larger than this diameter and 50% smaller.

horizontal two-ply knitting yarn lines set at 90, 180, 270, 360 and 450 mm below nozzle height. Recovered sodium fluorescein tracer was quantified by spectrofluorimetry.³

Oil emulsions and emulsifier alone reduced drift considerably (379 to 647 μg g⁻¹ tracer applied) compared with the aqueous surfactant (1070 μg g⁻¹ tracer applied). For example, drift from the ARRO EC at 10 g litre⁻¹ was less than 33% of that recorded with the

surfactant (Fig 1). There was a tendency for drift to increase with increasing oil concentration, whereas the reverse was true for the emulsifier. The mineral oil was the least efficient in controlling drift, giving 75% of that recorded for the surfactant solution.

Droplet-size was measured using an Aerometrics phase-Doppler particle analyser (PDPA)⁴ tracking through the centre of the long axis of the fan produced by a single stainless steel Lurmark 11002 nozzle

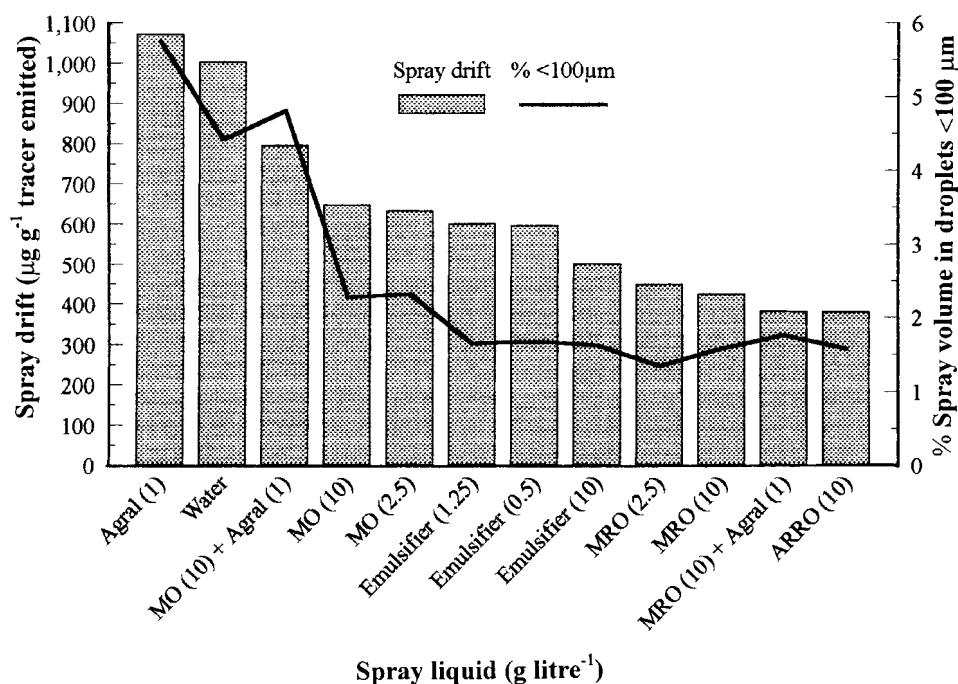


Figure 1. Effect of oil-based adjuvants on % spray volume in droplets of <100 μm diameter and spray drift measured at 2 m downwind in a wind speed of 2.5 ms⁻¹.

delivering 0.64 litre min⁻¹. The nozzle was positioned 350 mm above the laser crossover and each of three replicate measurements consisted of two sweeps through the spray cloud. In addition to the three oil emulsions, the droplet spectra from water, 1 g litre⁻¹ aqueous Agral and aqueous emulsifier at the three concentrations corresponding to the amounts present in the diluted oil ECs were measured. In addition, 1 g litre⁻¹ Agral was added to 10 g litre⁻¹ emulsions of MRO and MO to simulate the possible interaction between an emulsified oil and a pesticide containing a wetting agent.

In-flight PDPA measurements of the spray cloud showed that all of the oil-in-water emulsions increased droplet volume median diameters (VMD) when compared with water and the aqueous surfactant solution (Table 1). For example, 10 g litre⁻¹ MRO increased the VMD by 32% (247 to 326 µm) when compared with aqueous Agral. Emulsions of MO (10 g litre⁻¹) produced greater volumes of driftable droplets than similar concentrations of the two vegetable oils (2.27% cf 1.57 and 1.58% for ARRO and MRO, respectively). The addition of 1 g litre⁻¹ Agral to 10 g litre⁻¹ emulsions of mineral oil and MRO increased the potential of both to drift but this effect was more obvious with the mineral oil than with the vegetable oils.

Good agreement was observed between in-flight droplet-size measurements and drift data for most of the formulations. Oil emulsions and the emulsifier alone increased VMDs and decreased the proportion of driftable droplets with diameters less than 100 µm, compared with water and the surfactant solution. The surfactant generated the largest proportion of driftable droplets (5.75%) and 2.5 g litre⁻¹ MRO the smallest (1.34%), in accordance with their wind-tunnel drift potentials.

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Novel 1,3,5-triazine derivatives with herbicidal activity

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Abstract: New fluoroalkyl-substituted 1,3,5-triazine derivatives were synthesized and screened for herbicidal activity using a greenhouse pot test. Surprisingly, a series of 2-alkyl-4-fluoroalkyl-6-aralkylamino-1,3,5-triazines e.g. 6-(4-bromobenzylamino)-2-methyl-4-trifluoromethyl-1,3,5-triazine was found to possess strong pre- and post-emergence herbicidal activities, although the conventional herbicidal 1,3,5-triazines generally should have a 2-substituted-4,6-diamino-1,3,5-triazine structure for herbicidal activity. Our compounds show strong Photosynthetic Electron Transport inhibitory activity (PI₅₀ c 7). Although their herbicidal effect is considered to be caused by a process similar to that for the conventional 1,3,5-triazine herbicide atrazine, they can control atrazine-resistant *Chenopodium album* effectively, and will thus form promising trial compounds for new triazine herbicide design.

Keywords: 2-alkyl-4-fluoroalkyl-6-aralkylamino-1,3,5-triazines; herbicidal activity

1 INTRODUCTION

The 1,3,5-triazine skeleton is classical and one of the most interesting chemical core structures for biological activity, many triazine derivatives having been developed as agrochemicals, especially herbicides. However, most of these triazines are derivatives of cyanuric chloride simply substituted with nucleophilic reagents, and other types of triazines are not so well known. We have attempted to synthesize new types of triazine derivatives in order to find lead compounds for biological activity, starting from fluoroalkyl-substituted 1,3,5-triazine intermediates.¹ Through this approach, we found new herbicidal triazine derivatives of the type shown in Fig 1.²

2 EXPERIMENTAL AND RESULTS

The triazine derivatives were readily synthesized by reacting the fluoroalkyl-substituted 1,3,5-triazine in-

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